PCT/GB 2003 / 0 0 1 5 2 0

INVESTOR IN PEOPLE

The Patent Office
Concept House
Cardiff Road
Newport REC'D 2.1 MAY 2003
South Wales
NP10 8QQ WIPO PCT

I, the undersigned, being an officer duly authorised in accordance with Section 74(1) and (4) of the Deregulation & Contracting Out Act 1994, to sign and issue certificates on behalf of the Comptroller-General, hereby certify that annexed hereto is a true copy of the documents as originally filed in connection with the patent application identified therein.

In accordance with the Patents (Companies Re-registration) Rules 1982, if a company named in this certificate and any accompanying documents has re-registered under the Companies Act 1980 with the same name as that with which it was registered immediately before re-registration save for the substitution as, or inclusion as, the last part of the name of the words "public limited company" or their equivalents in Welsh, references to the name of the company in this certificate and any accompanying documents shall be treated as references to the name with which it is so re-registered.

In accordance with the rules, the words "public limited company" may be replaced by p.l.c., plc, P.L.C. or PLC.

Re-registration under the Companies Act does not constitute a new legal entity but merely subjects the company to certain additional company law rules.
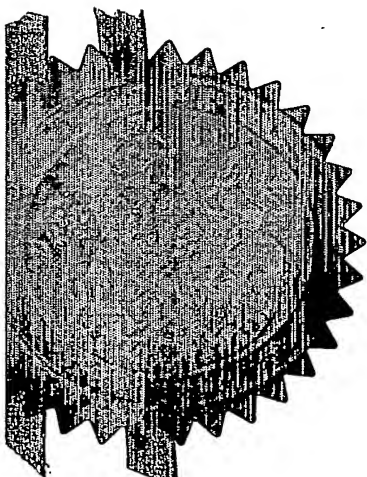
PRIORITY DOCUMENT
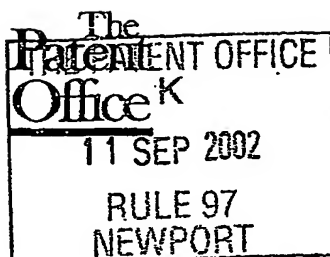SUBMITTED OR TRANSMITTED IN COMPLIANCE WITH RULE 17.1(a) OR (b)

Signed *Andrew Gregory*

Dated 25 April 2003

Patents Form 1/77

Pate( ) ct 1977
(Rule 16)

Request for grant of a patent

(See the notes on the back of this form. You can also get an explanatory leaflet from the Patent Office to help you fill in this form)

The Patent Office

Cardiff Road
Newport
Gwent NP9 1RH

1.	Your reference	SMC 60541/GB/P1

2.	Patent application number *(The Patent Office will fill in this part)*	11 SEP 2002 **0221090.4**

3.	Full name, address and postcode of the or of each applicant *(underline all surnames)*	Avecia Limited Hexagon House Blackley Manchester, M9 8ZS
	Patents ADP number *(if you know it)*	07764137001
	If the applicant is a corporate body, give the country/state of its incorporation	GB

4.	Title of the invention	PROCESS FOR CHEMICALLY PRODUCED TONER

5.	Name of your agent *(if you have one)*	PARLETT, Peter Michael
	"Address for service" in the United Kingdom to which all correspondence should be sent *(including the postcode)*	Avecia Limited Hexagon House Blackley Manchester, M9 8ZS United Kingdom
	Patents ADP number *(if you know it)*	084636 55001

		Country	Priority application number *(if you know it)*	Date of filing *(day / month / year)*
6.	If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and *(if you know it)* the or each application number			

		Number of earlier application	Date of filing *(day / month / year)*
7.	If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application		

8.	Is a statement of inventorship and of right to grant of a patent required in support of this request? *(Answer 'Yes' if:* a) *any applicant named in part 3 is not an inventor, or* b) *there is an inventor who is not named as an applicant, or* c) *any named applicant is a corporate body.* *See note (d))*	Yes

SMC 60541

APPLICANTS

AVECIA LIMITED

TITLE

PROCESS FOR CHEMICALLY PRODUCED TONER

PROCESS FOR CHEMICALLY PRODUCED TONER

Field of the invention

This invention relates to chemically produced toners for use in the formation of
5   electrostatic images, their process of manufacture, processes using them and to toner
apparatus and components incorporating them. It further relates to any
electroreprographic apparatus, component of the apparatus and consumable for use with
the apparatus, which comprises such a toner, and to methods of manufacturing of such
electroreprographic apparatus, components and consumables.
10

Related background art

Toners for development of an electrostatic image are conventionally produced by
melt kneading of a pigment, resin and other toner ingredients, followed by pulverisation.
Classification is then needed to generate an acceptably narrow particle size distribution.
15   Recently attention has been focussed on chemical routes to toners, where a
suitable particle size is not attained by a milling process, which avoid the need for a
classification step. By avoiding the classification step, higher yields can be attained,
especially as the target particle size is reduced. Lower particle size toners are of
considerable interest for a number of reasons, including better print resolution, lower pile
20   height, greater yield from a toner cartridge, faster or lower temperature fusing, and lower
paper curl.

Several routes to chemical toners have been exemplified. These include
suspension polymerisation, solution-dispersion processes and aggregation routes.
Aggregation processes offer several advantages including the generation of narrow
25   particle size distributions, and the ability to make toners of different shape. The toner
shape is particularly important in toner transfer from the organic photoconductor (OPC) to
the substrate, and in cleaning of the OPC by a blade cleaner.

Several aggregation processes have been reported. US 4996127 (Nippon
Carbide) reports a process in which black toner particles are grown by heating and stirring
30   resin particles made by emulsion polymerisation with a dispersion of carbon black, where
the resin contains acidic or basic polar groups. Numerous patents from Xerox (e.g. US
5418108) describe a flocculation process where particles stabilised by anionic surfactants
are mixed with particles stabilised by cationic surfactants (or where a cationic surfactant is
added to particles stabilised by an anionic surfactant). US 5066560 and US 4983488
35   (Hitachi Chemical Co.) describe emulsion polymerisation in the presence of a pigment,
followed by coagulation with an inorganic salt, such as magnesium sulphate or aluminium
chloride. The applicants' own patent applications WO 98/50828 and WO 99/50714,
describe aggregation processes in which a surfactant used to stabilise the latex (i.e. the
aqueous dispersion of the resin) and pigment is converted by a pH change from an ionic
40   to a non-ionic state, so initiating flocculation.

To form a permanent image on the substrate, it is necessary to fuse or fix the toner particles to the substrate. This is commonly achieved by passing the unfused image between two rollers, with at least one of the rollers heated. It is important that the toner does not adhere to the fuser rollers during the fixation process. Common failure modes include paper wrapping (where the paper follows the path of the roller) and offset (where the toner image is transferred to the fuser roller, and then back to a different part of the paper, or to another paper sheet). One solution to these problems is to apply a release fluid, e.g. a silicone oil, to the fuser rollers. However this has many disadvantages, in that the oil remains on the page after fusing, problems can be encountered in duplex (double-sided) printing, and the operator must periodically re-fill the oil dispenser. These problems have led to a demand for so-called "oil-less" fusion, in which a wax incorporated in the toner melts during contact of the toner with the heated fuser rollers. The molten wax acts as a release agent, and removes the need for application of the silicone oil.

There are many problems associated with the inclusion of wax in a toner. Wax present at the surface of the toner may affect the triboelectric charging and flow properties, and may reduce the storage stability of the toner by leading to toner blocking. Another problem frequently encountered is filming of the wax onto the metering blade and development rollers (for mono-component printers) or the carrier bead (for dual-component printers or copiers), and onto the photoconductor drum. Where contact charging and/or contact development are employed, and where cleaning blades or rollers are used, these can place an extra stress on the toner and make it more prone to filming. If the wax is not well dispersed in the toner problems with transparency in colour toners can be found, and high haze values result. With conventional toners, prepared by the extrusion/pulverisation route, it has only proved possible to introduce relatively small amounts of wax without encountering the above problems.

With colour toners, the demands on the toner to achieve oil-less release are much more severe than with monochrome printing. As typically four colours are used in full-colour printing, the mass of toner which can be deposited per unit area is much higher than with black printing. Print densities of up to around 2 mg/cm^2 may be encountered in colour printing, compared with about 0.4-0.7 mg/cm^2 in monochrome prints. As the layer thickness increases it becomes more difficult to melt the wax and obtain satisfactory release at acceptable fusion temperatures and speeds. Of course it is highly desirable to minimise the fusion temperature, as this results in lower energy consumption and a longer fuser lifetime. With colour printing it is also important that prints show high transparency. In addition it is necessary to be able to control the gloss level. Inclusion of waxes in colour toners can have detrimental effects on transparency, and can make it difficult to reach higher gloss levels.

The efficiency of wax melting can be increased by reducing the wax melting point. However this often leads to increased storage-stability problems, and in more pronounced filming of the OPC or metering blade. The domain size of the wax is also important, as this affects the release, storage stability and transparency of the toner.

The release properties of the toner can also be affected by the molecular weight distribution of the toner. Broader molecular weight distribution toners, which include a proportion of higher molecular weight (or alternatively cross-linked resin), generally show greater resistance to offset at higher fusion temperatures. However, when large amounts

5 of high molecular weight resins are included, the melt viscosity of the toner increases, which requires a higher fusion temperature to achieve fixation to the substrate and transparency. The haze values of the prints will then vary considerably with fusion temperature, with unacceptably high values at low fusion temperatures. Haze may be assessed using a spectrophotometer, for example a Minolta CM-3600d, following ASTM D

10 1003.

Therefore the requirements for achieving an oil-less fusion colour system are severe. It is necessary to achieve a reasonably low fusion temperature, with an acceptably wide release temperature window, including with high print densities. The prints must show good transparency with controllable gloss. The toner must not show

15 blocking under normal storage conditions, and must not lead to filming of the OPC or metering blade.

In addition it is important that the quality of the prints is maintained over a long print run, and that the toner is efficiently used. To achieve these goals there must be little development of the non-image areas of the photoconductor (OPC) and the toner must

20 show a high transfer efficiency from the photoconductor to the substrate (or to an intermediate transfer belt or roller). If the transfer efficiency is close to 100% it is possible to avoid the need for a cleaning step, where residual toner is removed from the photoconductor after transfer of the image. However many electrophotographic devices contain a mechanical cleaning device (such as a blade or a roller) to remove any residual

25 toner from the photoconductor. Such residual toner may arise either from development of the non-image areas of the photoconductor, or from incomplete transfer from the photoconductor to the substrate or intermediate transfer belt or roller. A high transfer efficiency is especially important for colour devices, where usually more than one transfer step is required (for example from the photoconductor to a transfer belt or roller, and

30 subsequently from the transfer belt or roller to the substrate).

It is known in the art that the shape of the toner can have a pronounced effect on its transfer and cleaning properties. Toners prepared by conventional milling techniques tend to have only moderate transfer efficiencies due to their irregular shape. Spherical toners may be prepared by chemical routes, such as by suspension polymerisation or by

35 latex aggregation methods. These toners can transfer well, but the efficiency of cleaning with mechanical cleaning devices such as cleaning blades is low.

It is therefore desirable to produce a toner which can satisfy many requirements simultaneously. The toner should be capable of fixing to the substrate at low temperatures by means of heated fusion rollers where no release oil is applied. The toner should be

40 capable of releasing from the fusion rollers over a wide range of fusion temperatures and speeds, and over a wide range of toner print densities. To achieve this it is necessary to

●   4   ●

include a wax or other internal release agent in the toner. This release agent must not cause detrimental effects on storage stability, print transparency or toner charging characteristics, and must not lead to background development of the photoconductor (OPC). It must also not lead to filming of the metering blade or development roller (for a mono-component device) or the carrier bead (for a dual- component device), or of the photoconductor. In addition the shape of the toner must be controlled so as to give high transfer efficiency from the photoconductor to the substrate or intermediate transfer belt or roller, and from the transfer belt or roller (where used) to the substrate. If a mechanical cleaning device is used the shape of the toner must also be such as to ensure efficient cleaning of any residual toner remaining after image transfer.

Several patents exemplify aggregation processes where a single latex, made by a one-stage emulsion polymerisation process, is aggregated with a wax dispersion. Examples where a system based on counterionic surfactants (i.e. an anionic and a cationic surfactant) is used include US 5994020 and US 5482812 (both to Xerox). Examples where an inorganic coagulant is used include US 5994020, US 6120967, US 6268103 and US 6268102 (all to Xerox). Mixed inorganic and organic coagulants are used in US 6190820 and US 6210853 (both to Xerox). US 4996127 (Nippon Carbide) exemplifies a process in which a latex containing an acidic-functional group is heated and stirred with a wax dispersion and carbon black to grow aggregate toner particles.

US 5928830 (Xerox) discloses a two stage emulsion polymerisation to make a core shell latex. The shell is made generally of higher molecular weight and/or Tg than the core. The latex is then mixed with pigment and flocculated through use of counterionic surfactants. Inclusion of wax is not exemplified.

US 5496676 (Xerox) discloses use of blends of different latexes with different molecular weight to increase the fusion latitude. Each latex is made by a single stage polymerisation. Toners were made by flocculating the mixed latexes with a pigment dispersion containing a counterionic surfactant. Inclusion of wax is not exemplified.

In US 5965316 (Xerox) encapsulated waxes are made by carrying out the emulsion polymerisation in the presence of a wax dispersion. These emulsion polymers containing wax are mixed with non wax containing latexes of similar molecular weight, and toners made using a counterionic flocculation route.

JP 2000-35690 and JP 2000-98654 describe aggregation processes where a non-ionically stabilised dispersion of an ester-type wax is aggregated with mixed polymer emulsions of different molecular weight.

US 5910389, US 6096465 and US 6214510 (Fuji Xerox) disclose blends of resins with different molecular weights, incorporating hydrocarbon waxes of melting point ~ 85°C. US 6251556 (Fuji Xerox) also discloses blends of resins, as well as a two stage emulsion polymerisation to make a core shell latex. The only wax which is incorporated is a high melting point (160 °C) polypropylene wax.

Control over the toner particle shape in aggregation processes has been demonstrated. US 5501935 and US 6268102 (Xerox) both exemplify spherical particles.

Toners which are non-spherical, but have low shape factors are disclosed in US 6268103 (Xerox); US 6340549, US 6333131, US 6096465, US 6214510 and US 6042979 (Fuji Xerox); and US 5830617 and US 6296980 (Konica). Advantages of lower shape factors in improving transfer efficiency are shown in US 6214510 and US 6042979 (Fuji Xerox) and
5 US 5830617 (Konica). However, none of these references discloses a toner for use in a mono-component electroreprographic apparatus which is capable of demonstrating: release from oil-less fusion rollers over a wide range of fusion temperature and print density; high transparency for OHP slides over a wide range of fusion temperature and print density; high transfer efficiency and the ability to clean any residual toner from the
10 photoconductor, and the absence of filming of the metering blade, development roller and photoconductor over a long print run.

Summary of the invention
        Therefore, obtaining a suitable toner, and a process for making it, which meets all
15 the above requirements is difficult and requires careful selection of the many possible components and parameters, each of which has constraints imposed on its physical and chemical properties by the final parameters of the system.
        According to the present invention there is provided a toner for developing an electrostatic image comprising a binder resin, a wax and a colorant, characterised in that
20 the toner is made by flocculating a dispersion of the resin (latex), a dispersion of the wax and a dispersion of the colorant, followed by heating and stirring to form composite particles containing the resin, wax and colorant, and then coalescing these particles above the Tg of the resin, wherein the wax has a melting point of between 50 and 150°C, and the coalescence stage is controlled, such that:
25   (a) the mean circularity of the coalesced particles as measured by a Flow Particle Image Analyser is at least 0.90;
            (b) the shape factor (SF) of the coalesced particles is at most 165; and
            (c) the wax exists in the coalesced particles in domains of 2 μm or less mean particle size.
30   The mean circularity of the coalesced particles as measured by a Flow Particle Image Analyser is preferably at least 0.93, more preferably at least 0.94.
        The shape factor (SF) of the coalesced particles is preferably at most 155, more preferably at most 145.
        The resin may have a ratio of weight average molecular weight (Mw) to number
35 average molecular weight of at least 3, preferably at least 5, more preferably at least 10.
        We have found that by using an aggregation process with particular wax dispersions, it is possible to incorporate wax in relatively high amounts (e.g. about 5-15 wt%) without problems of blocking or filming, and without adverse effects on toner flow or tribocharge, or on print transparency. The wax is present in the toner in domains of mean
40 diameter 2μm or less, preferably 1.5μm or less. Preferably, the wax domains are of mean diameter 0.5μm or greater. Preferably the wax is not substantially present at the surface of

the toner. The relatively high wax levels allow oil-less release even at high print densities, without requiring excessive amounts of high weight average molecular weight (M_w) resin. This allows fixation at low temperatures, and high transparency across a range of fusion temperatures. To achieve satisfactory oil-less release at high temperatures, it is necessary to have present polymer chains encompassing a wide range of molecular weights. This can be achieved either by mixing resin particles of widely different molecular weight, or by synthesising a latex (i.e. an aqueous dispersion of resin) containing a broad molecular weight distribution. A combination of both approaches can be used.

Latexes may be made by polymerisation processes known in the art, preferably by emulsion polymerisation. The molecular weight can be controlled by use of a chain transfer agent (e.g. a mercaptan), by control of initiator concentration or by heating time. Preferably, the binder resin is prepared from at least one latex with monomodal molecular weight distribution and at least one latex with bimodal molecular weight distribution. Latexes with a bimodal molecular weight distribution may be made using a two-stage polymerisation. Preferably a higher molecular weight resin is made first, then in a second stage, a lower molecular weight resin is made in the presence of the first resin. As a result, a bimodal molecular weight distribution resin is made containing both low and high molecular weight resins. This may then be mixed with a monomodal low molecular weight resin. In a further aspect of the invention, three latexes can be used, where preferably at least two of these show bimodal molecular weight distributions. In a further preference, the second bimodal latex is of higher molecular weight than the first.

Preferably, the monomodal molecular weight latex is a low molecular weight latex and has a number average molecular weight of from 3000 to 10000, more preferably from 3000 to 6000. Where the binder resin is prepared from one bimodal latex, the bimodal latex preferably has a weight average molecular weight of from 100,000 to 500,000, more preferably from 200,000 to 400,000. Where the binder resin is prepared from more than one bimodal latex, one bimodal latex may optionally have a weight average molecular weight from 500,000 to 1,000,000 or more.

The higher molecular weight resins may also contain cross-linked material by inclusion of a multifunctional monomer (e.g. divinylbenzene or a multi-functional acrylate) It is preferred that the overall molecular weight distribution of the toner resin shows M_w/M_n of 3 or more, more preferably 5 or more. The Tg of each resin is preferably from 30 to 100 °C, more preferably from 45 to 75 °C, most preferably from 50 to 70 °C. If the Tg is too low, the storage stability of the toner will be reduced. If the Tg is too high, the melt viscosity of the resin will be raised, which will increase the fixation temperature and the temperature required to achieve adequate transparency. It is preferred that all the components in the resin have a substantially similar Tg.

The resin may include one or more of the following preferred monomers for emulsion polymerisation: styrene and substituted styrenes ; acrylate and methacrylate alkyl esters (e.g. butyl acrylate, butyl methacrylate, methyl acrylate, methyl methacrylate, ethyl acrylate or methacrylate, octyl acrylate or methacrylate, dodecyl acrylate or

methacrylate etc.) ; acrylate or methacrylate esters with polar functionality, for example hydroxy or carboxylic acid functionality, hydroxy functionality being preferred (particularly 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, or hydroxy-terminated poly(ethylene oxide) acrylates or methacrylates, or hydroxy-terminated poly(propylene oxide) acrylates or methacrylates), examples of monomers with carboxylic acid functionality including acrylic acid and beta-carboxyethylacrylate ; vinyl type monomers such as ethylene, propylene, butylene, isoprene and butadiene ; vinyl esters such as vinyl acetate ; other monomers such as acrylonitrile, maleic anhydride, vinyl ethers.

Preferred resins are copolymers of (i) a styrene or substituted styrene, (ii) at least one alkyl acrylate or methacrylate and (iii) an hydroxy-functional acrylate or methacrylate.

The resin may be prepared from the following, not used in emulsion polymerisation: dispersions of polyesters, polyurethanes, hydrocarbon polymers, silicone polymers, polyamides, epoxy resins etc.

Preferably, the latex is a dispersion in water. Optionally the latex dispersion further comprises an ionic surfactant; preferably the surfactant present on the dispersions contains a group which can be converted from an ionic to a non-ionic form by adjustment of pH. Preferred groups include carboxylic acids or tertiary amines. Preferably, the ionic surfactant has a charge of the same sign (anionic or cationic) as that of the surfactant used in the wax and colorant dispersions described below. Optionally a non-ionic surfactant may also be incorporated into the latex dispersion.

The wax should have a melting point (mpt) (as measured by the peak position by differential scanning calorimetry (dsc)) of from 50 to 150°C, preferably from 50 to 130°C, more preferably from 50 to 110 °C, especially from 65 to 85 °C. If the mpt is >150°C the release properties at lower temperatures are inferior, especially where high print densities are used. If the mpt is <50°C the storage stability of the toner will suffer, and the toner may be more prone to showing filming of the OPC or metering blade.

In a further embodiment of the invention, the wax is made as a dispersion in water, preferably stabilised with an ionic surfactant. The ionic surfactant is selected from the same classes as described above for the latex dispersion; preferably, the ionic surfactant has the same sign (anionic or cationic) as the surfactant used for the latex dispersion described above and the colorant dispersion described below. The mean volume particle size of the wax in the dispersion is preferably in the range from 100nm to 2 µm, more preferably from 200 to 800 nm, most preferably from 300 to 600 nm, and especially from 350 to 450 nm. The wax particle size is chosen such that an even and consistent incorporation into the toner is achieved. The wax should be present in the toner in domains, where the mean size of the domains is at most 2 µm, preferably 1.5 µm or less. If the mean size of the wax domains is > 2 µm, the transparency of the printed film may be reduced, and the storage stability may decrease. The particle size values given are those measured by a Coulter LS230 Particle Size Analyser (laser diffraction) and are the volume mean.

The wax may comprise any conventionally used wax. Examples include hydrocarbon waxes (e.g. polyethylenes such as Polywax™ 400, 500, 600, 655, 725, 850, 1000, 2000 and 3000 from Baker Petrolite; paraffin waxes and waxes made from CO and H_2 , especially Fischer-Tropsch waxes such as Paraflint™ C80 and H1 from Sasol; ester

5   waxes, including natural waxes such as Carnauba and Montan waxes; amide waxes; and mixtures of these. Hydrocarbon waxes are preferred, especially Fischer-Tropsch and paraffin waxes. It is especially preferred to use a mixture of Fischer-Tropsch and Carnauba waxes, or a mixture of paraffin and Carnauba waxes.

The amount of wax incorporated in the toner is preferably from 1 to 30 wt% based

10   on the total weight of toner, more preferably from 3 to 20 wt%, especially from 5 to 15 wt%. If the level of wax is too low, the release properties will be inadequate for oil-less fusion. Too high a level of wax will reduce storage stability and lead to filming problems. The distribution of the wax through the toner is also an important factor, it being preferred that wax is not present at the surface of the toner.

15   Advantageously, the toner is capable of fixing to the substrate at low temperatures by means of heated fusion rollers where no release oil is applied and is capable of releasing from the fusion rollers over a wide range of fusion temperatures and speeds, and over a wide range of toner print densities. Furthermore, it has been found that the toner according to the invention does not lead to background development of the

20   photoconductor (OPC) and does not lead to filming of the metering blade or development roller (for a mono-component device) or the carrier bead (for a dual- component device), or of the photoconductor.

Advantageously, the haze values of prints using the toner of the invention do not vary considerably with fusion temperature. Haze may be assessed using a

25   spectrophotometer, for example a Minolta CM-3600d, following ASTM D 1003. Preferably, the haze at a print density of 1.0 mg/cm^2 is below 40, and the ratio of the values at fusion temperatures of 130 and 160°C is preferably at most 1.5 , more preferably 1.3 and most preferably 1.2.

Accordingly, the invention in another aspect provides a process for forming an

30   image, the process comprising developing an electrostatic image using a toner according to the invention, wherein the haze at a print density of 1.0 mg/cm^2 is below 40, and the ratio of the values at fusion temperatures of 130 and 160°C is at most 1.5 , preferably 1.3 and more preferably 1.2. The fusion speed in the process may be at least 10 pages per minute, preferably at least 20 pages per minute.

35   Preferably the colorant comprises a pigment. Any suitable pigment can be used, including black and magnetic pigments. For example carbon black, magnetite, copper phthalocyanine, quinacridones, xanthenes, mono- and dis-azo pigments, naphthols etc. Examples include Pigment Blue 15:3, Red 31, 57, 81, 122, 146, 147 or 184; Yellow 12, 13, 17, 74, 180 or 185. Preferably, the colorant is milled with an ionic surfactant, and

40   optionally a non-ionic surfactant until the particle size is reduced, preferably to <300 nm, more preferably <100 nm. In full colour printing it is normal to use yellow, magenta, cyan

and black toners. However it is possible to make specific toners for spot colour or custom colour applications. When the colorant is milled with an ionic surfactant, the surfactant is preferably selected from the same classes of surfactant described above for the binder resin and the wax; more preferably the surfactant has the same sign as both the surfactants used above. The colorant dispersion is also preferably a dispersion in water.

The toner as described above may additionally optionally comprise a charge control agent (CCA); preferably the charge control agent has been milled with the colorant. Suitable charge control agents are preferably colourless. Preferably, they include metal complexes, more preferably aluminium or zinc complexes, phenolic resins etc. Examples include Bontron^{TM} E84, E88, E89 and F21 from Orient; Kayacharge N1, N3 and N4 from Nippon Kayaku; LR147 from Japan Carlit; TN-105 from Hodogaya. These can be milled in a similar manner to the pigment. Where the CCA is added externally, a suitable high-speed blender may be used, e.g. a Nara Hybridiser. Alternatively, the CCA may be added as part of the pre-flocculation mixture, preferably as a wet cake.

According to the present invention, there is also provided a process for the manufacture of a toner according to the above which comprises the following steps:

    i.   preparing a latex dispersion;

    ii.   preparing a wax dispersion;

    iii.   preparing a colorant dispersion;

    iv.   mixing the latex dispersion, wax dispersion and colorant dispersion; and

    v.   causing the mixture to flocculate.

The process may further comprise, prior to step iv, the additional step of preparing a charge control agent component, which component may then be incorporated in step iv by mixing. The charge control agent may be milled with the colorant.

Preferably, each dispersion is a dispersion in water.

The latex dispersion preferably comprises an ionic surfactant. More preferably the preparation of the latex dispersion comprises mixing together at least one latex with monomodal molecular weight distribution and at least one latex with bimodal molecular weight distribution. The preparation of the latex with bimodal molecular weight distribution preferably comprises the successive steps of formation of a resin of high molecular weight distribution followed by formation of a resin of low molecular weight distribution such that the resulting latex comprises composite particles comprising both the said low molecular weight resin and the said high molecular weight resin. The preparation of the wax dispersion in such a process preferably comprises the mixing together of the wax with an ionic surfactant. The preparation of the colorant dispersion in such a process preferably comprises the milling together of the colorant with an ionic surfactant.

It is preferred that the dispersions of latex, colorant, charge control agent where present, and wax have the same sign charge on the surfactant. This enables individual components to be well mixed prior to flocculation. It is further preferred to use the same surfactant for each of the individual dispersions. The mixed dispersions are then flocculated in step (v). Any suitable method could be used, e.g. addition of an inorganic

salt, an organic coagulant, or by heating and stirring. In a preferred method, the surfactant present on the dispersions contains a group which can be converted from an ionic to a non-ionic form and vice versa by adjustment of pH. In a preferred example, the surfactant may contain a carboxylic acid group, and the dispersions may be mixed at neutral to high pH. Flocculation may then be effected by addition of an acid, which converts the surfactant from anionic to non-ionic. Alternatively the surfactant can be the acid salt of a tertiary amine, used at low pH. Flocculation may then be effected by addition of a base which converts the surfactant from cationic to non-ionic form. The flocculation step is preferably carried out below the Tg of the resin, but the mixed dispersions may be heated prior to flocculation. Such processes as described above, allow a very efficient use of surfactant, and the ability to keep overall surfactant levels very low. This is advantageous since residual surfactant can be problematic, especially in affecting the charging properties of the toner, particularly at high humidity. In addition, such processes avoid the need for large quantities of salt, as required for many prior art processes, which would need to be washed out.

After the flocculation step (v), the process as described above may optionally comprise heating the flocculated mixture to form loose aggregates of particle size from 3 to 20 µm. Once the correct particle size is established, the aggregates may be stabilised against further growth. This may be achieved, for example, by addition of further surfactant, and/or by a change in pH. The temperature may then be raised above the T_g of the resin to bring about coalescence of the particles within each aggregate. During this step the shape of the toner may be controlled through selection of the temperature and the heating time.

The shape of the toner may be measured by use of a Flow Particle Image Analyser (Sysmex FPIA) and by image analysis of images generated by scanning electron microscopy (SEM).

The circularity is defined as the ratio :

$$Lo/L$$

where Lo is the circumference of a circle of equivalent area to the particle, and L is the perimeter of the particle itself.

The shape factor (SF) is defined as:

$$SF = \frac{(maximum\ diameter)^2 \times 100\pi/4}{area}$$

An average of approximately 100 particles is taken to define the shape factor for the toner.

If the toner is designed for a printer or copier which does not employ a mechanical cleaning device, it may be preferred to coalesce the toner until a substantially spherical shape is attained. If, however, the toner is designed for use in a printer or copier in which

a mechanical cleaning device is employed to remove residual toner from the photoconductor after image transfer, it may be preferred to select a smooth off-spherical shape, where the mean circularity is in the range 0.90-0.99, preferably 0.93-0.99, more preferably 0.94-0.99, and with a SF 105-165, preferably 105-155, more preferably 105-
5   145.

The smoothness of the toner after the coalescence stage may also be assessed by measuring the surface area of the toner, for example by the BET method. It is preferred that the BET surface area of the unformulated toner is in the range 0.5-1.5 m^2/g, preferably 0.6-1.3 m^2/g, more preferably 0.7-1.1 m^2/g. By unformulated is meant the toner
10   prior to any optional blending with surface additives.

Advantageously, the manner of making the toner according to the invention enables the shape of the toner to be controlled so as to give both high transfer efficiency from the photoconductor to the substrate or intermediate transfer belt or roller, and from the transfer belt or roller (where used) to the substrate, as well as to ensure efficient
15   cleaning of any residual toner remaining after image transfer.

The cooled dispersion of coloured resin particles is then optionally washed to remove surfactant, and then dried.

The particles may then be blended with one or more surface additives to improve the powder flow properties of the toner, or to tune the tribocharge properties. Typical
20   surface additives include, but are not limited to, silica, metal oxides such as titania and alumina, polymeric beads (for example acrylic or fluoropolymer beads) and metal stearates (for example zinc stearate). Conducting additive particles may also be used, including those based on tin oxide (e.g. those containing antimony tin oxide or indium tin oxide). The additive particles, including silica, titania and alumina, may be made
25   hydrophobic, e.g. by reaction with a silane and/or a silicone polymer. Examples of hydrophobising groups include alkyl halosilanes, aryl halosilanes, alkyl alkoxysilanes (e.g. butyl trimethoxysilane, iso-butyl trimethoxysilane and octyl trimethoxysilane), aryl alkoxysilanes, hexamethyldisilazane, dimethylpolysiloxane and octamethylcyclotetrasiloxane. Other hydrophobising groups include those containing
30   amine or ammonium groups. Mixtures of hydrophobising groups can be used (for example mixtures of silicone and silane groups, or alkylsilanes and aminoalkylsilanes.)

Examples of hydrophobic silicas include those commercially available from Nippon Aerosil, Degussa, Wacker-Chemie and Cabot Corporation. Specific examples include those made by reaction with dimethyldichlorosilane (e.g. Aerosil^{TM} R972, R974
35   and R976 from Degussa); those made by reaction with dimethylpolysiloxane (e.g. Aerosil^{TM} RY50, NY50, RY200, RY200S and R202 from Degussa); those made by reaction with hexamethyldisilazane (e.g. Aerosil^{TM} RX50, NAX50, RX200, RX300, R812 and R812S from Degussa); those made by reaction with alkylsilanes (e.g. Aerosil^{TM} R805 and R816 from Degussa) and those made by reaction with octamethylcyclotetrasiloxane
40   (e.g. Aerosil^{TM} R104 and R106 from Degussa).

The primary particle size of the silicas used is typically from 5 to 100nm, preferably from 7 to 50 nm. The BET surface area may be from 20 to 350 m^2/g, preferably 30-300 m^2/g. Combinations of silicas with different particle size and/or surface area may be used. Preferred examples of combinations of silicas with different primary particle size are: Aerosil™ R972 (Degussa), or HDK™ H15 or H30 (Wacker); with Aerosil™ RX50, RY50 (Degussa) or HDK™ H05TD, H05TM or H05TX (Wacker). Each additive may be used at 0.1-5.0 wt% based on toner, preferably 0.2-3.0 wt.%, more preferably 0.25-2.0 wt%. It is possible to blend the different size additives in a single blending step, but it is often preferred to blend them in separate blending steps. In this case, the larger additive may be blended before or after the smaller additive. It may further be preferred to use two stages of blending, where in at least one stage a mixture of additives of different particle size is used. For example, an additive with low particle size may be used in the first stage, with a mixture of additives of different particle size in the second step. Examples would include use of Aerosil™ R812S or R972, or HDK™ H15 or H30 in the first step, along with a mixture containing one of these additives with a larger additive (such as Aerosil™ RX50 or RY50, or HDK™ H05TD, H05TM or H05TX) in the second step. In such a case it would be preferred to use 0.2-3.0 wt%, preferably 0.25-2.0 wt% of the smaller additive in the first step, and 0.1 to 3.0 wt%, preferably 0.2 to 2.0 wt% of each of the additives in the second step.

Where titania is used, it is preferred to use a grade which has been hydrophobised, e.g. by reaction with an alkylsilane and/or a silicone polymer. The titania may be crystalline or amorphous. Where crystalline it may consist of rutile or anatase structures, or mixtures of the two. Examples include grades T805 or NKT90 from Nippon Aerosil.

Hydrophilic or hydrophobic grades of alumina may be used. A preferred grade is Aluminium Oxide C from Degussa.

It is often preferred to use combinations of silica and titania (e.g. R972, H15, R812S or H30 with NKT90), or of silica, titania and alumina (e.g. R972, H15, R812S or H30 with NKT90 and Aluminium Oxide C). Combinations of large and small silicas, as described above, can be used in conjunction with titania, alumina, or with blends of titania and alumina. Preferred formulations include those in the following list:

hydrophobised silica ;

large and small particle size silica combinations;

hydrophobised silica and one or both of hydrophobised titania and hydrophilic or hydrophobised alumina ;

large and small particle size silica combinations as described above and one or both of hydrophobised titania and hydrophilic or hydrophobised alumina.

Polymer beads or zinc stearate may be used to improve the transfer efficiency or cleaning efficiency of the toners. Charge-control agents may be added in the external formulation to modify the charge level or charging rate of the toners.

●   13   ●

The total level of flow additives used may be from about 0.1 to about 10 wt%, preferably from about 0.5 to 5%, based on the weight of the base toner, i.e. prior to addition of the flow additive. The additives may be added by blending with the toner, using, for example, a Henschel blender, a Nara Hybridiser, or a Cyclomix blender (Hosokawa).

The toner may be used as a mono-component or a dual component developer. In the latter case the toner is mixed with a suitable carrier bead.

The invention is particularly suitable for use where one or more of the following hardware conditions of an electroreprographic device applies:

i)   where the device contains a developer roller and metering blade (i.e. where the toner is a monocomponent toner) ;

ii)   where the device contains a cleaning device for mechanically removing waste toner from the photoconductor ;

iii) where the photoconductor is charged by a contact charging means;

iv)   where contact development takes place;

v)   where oil-less fusion rollers are used;

vi)   where the above devices are four colour printers or copiers, including tandem machines

Advantageously, the invention provides a toner which satisfies many requirements simultaneously. The toner is particularly advantageous for use in a mono-component electroreprographic apparatus and is capable of demonstrating: release from oil-less fusion rollers over a wide range of fusion temperature and print density; high transparency for OHP slides over a wide range of fusion temperature and print density; high transfer efficiency and the ability to clean any residual toner from the photoconductor, and the absence of filming of the metering blade, development roller and photoconductor over a long print run.

In another aspect of the present invention, there is provided a process for manufacturing an electroreprographic apparatus and/or a component of the apparatus and/or a consumable for use with the apparatus, the process using a toner as described above.

In yet another aspect of the present invention, there is provided an electroreprographic apparatus, a component of the apparatus and/or a consumable for use with the apparatus, which comprises a toner as described above.

All weights referred to herein are percentages based on the total weight of the toner, unless otherwise stated.

The invention will now be illustrated by the following Examples, which are non-limiting on the invention.

1. Preparation of Latexes

1.1. Synthesis of Latex a –1

A low molecular weight resin was synthesised by emulsion polymerisation. The monomers used were styrene (83.2 wt%), 2-hydroxyethyl methacrylate (3.5 wt%) and acrylic ester monomers (13.3 wt%). Ammonium persulphate (0.5 wt% on monomers) was used as the initiator, and a mixture of thiol chain transfer agents (4.5 wt%) was used as chain transfer agents. The surfactant was Akypo™ (a carboxylated alkyl ethoxylate, i.e. a carboxy-functional surfactant) RLM100 (available from Kao, 3.0 wt% on monomers). The emulsion had a particle size of 93 nm, and a Tg midpoint (as measured by differential scanning calorimetry (dsc)) of 55 °C. GPC analysis against polystyrene standards showed the resin to have Mn = 6,500, Mw = 14,000, Mw/Mn = 2.2. The solids content was 30 wt%.

1.2 Synthesis of Latex a-2

A latex was made by a similar process to that used for Latex a-1. The emulsion had a particle size of 94 nm, and a Tg midpoint (as measured by differential scanning calorimetry (dsc)) of 53 °C. GPC analysis against polystyrene standards showed the resin to have Mn = 5,200, Mw = 14,000, Mw/Mn = 2.7. The solids content was 30 wt%.

1.3. Synthesis of Latex b-1

A bimodal molecular weight distribution latex was made by a two-stage polymerisation process, in which the higher molecular weight portion was made in the absence of chain transfer agent, and in which the molecular weight of the lower molecular weight portion was reduced by use of 2.5 wt% of mixed thiol chain transfer agents. Ammonium persulphate (0.5 wt% on monomers) was used as the initiator, and the surfactant was Akypo™ RLM100 (available from Kao, 3 wt% on monomers).

The monomer composition for the low molecular weight portion was styrene (82.5%, 2-hydroxyethyl methacrylate (2.5%) and acrylic ester monomers (15.0%). The overall monomer composition was styrene (73.85 wt%), 2-hydroxyethyl methacrylate (6.25 wt%) and acrylic ester monomers (19.9 wt%). The emulsion had a particle size of 78 nm and a Tg midpoint (as measured by dsc) of 67°C. GPC analysis against polystyrene standards showed a bimodal molecular weight distribution with Mn = 30,000, Mw = 249,000, Mw/Mn = 8.3. The solids content was 40 wt%.

1.4 Synthesis of Latex b-2

The latex was made in a similar manner to Latex b-1. The emulsion had a particle size of 77 nm and a Tg onset (as measured by dsc) of 58 °C. GPC analysis against polystyrene standards showed a bimodal molecular weight distribution with Mn = 26,000, Mw = 237,000, Mw/Mn = 9.1. The solids content was 40 wt%.

1.5 Synthesis of Latex b-3

The latex was made in a similar manner to Latex B-1. The emulsion had a particle size of 82 nm and a Tg midpoint (as measured by dsc) of 64°C. GPC analysis against

polystyrene standards showed a bimodal molecular weight distribution with Mn = 29,000, Mw = 250,000, Mw/Mn = 8.6. The solids content was 40 wt%.

2. Pigment dispersion

A dispersion of Pigment Red 122 (Hostaperm™ Pink E, Clariant) was used. The pigment was milled in water using a bead mill, with Akypo™ RLM100 (Kao) and Solsperse™ 27000 (Avecia) (a polymeric dispersant) as dispersants. The pigment content of the dispersion was 22.1 wt%.

3. Wax dispersion

An aqueous wax dispersion was used which contained an 80:20 mixture of Paraflint™ C80 (Fischer-Tropsch wax from Sasol) and Carnauba wax. Akypo™ RLM 100 was used as the dispersant. The mean volume particle size of the wax was approximately 0.4 μm, and the solids content 25 wt%. Analysis by differential scanning calorimetry (dsc) of the dried dispersion showed the wax to have a melting point (peak position from the dsc trace) of approximately 76 °C

4. Toner preparation

4.1 Toner example 1

Latex a-1 (7150 g), Latex b-1 (825 g) the wax dispersion (1429 g), the pigment dispersion (475 g, containing 105 g Pigment Red 122) and a paste of Bontron E88 (308 g, Orient, containing 60 g of Bontron E88) and water (19830 g) were mixed and stirred. The temperature was raised to 40°C. The mixed dispersions were circulated for 10 mins through a high shear mixer and back into the vessel. Then, as the material was circulating a solution of sulphuric acid was added into the high shear mixer to reduce the pH to 2.5. The temperature was then raised to 55°C, and stirring continued for 1 hr. A solution of sodium dodecybenzenesulphonate (750 g of a 10% solution) was added, and dilute sodium hydroxide solution was added to raise the pH to 7.3. The temperature was then raised to 120°C and stirring continued for a further 80 mins. Coulter Counter™ analysis showed the mean volume particle size was 8.7 μm and the final GSD was 1.25. Microscopic analysis showed the toner particles to be of uniform size and of smooth, off-spherical shape. Analysis with a Flow Particle Image Analyser (Sysmex FPIA,) showed the mean circularity to be 0.95

The resultant magenta toner dispersion was filtered on a pressure filter, and washed with water. The toner was then dried in an oven. Analysis by GPC against polystyrene standards, showed the toner resin to have Mn = 3,500, Mw = 50,600, Mw/Mn = 14.4.

Analysis by transmission electron microscopy (TEM) showed the presence of wax domains in the toner, the domain size being approximately 1.0-1.5 μm. BET surface area measurements showed the particles to have a surface area of 0.85 m²/g.

A portion of the toner was blended using a Prism blender with 0.5 wt % of Aerosil™ R812S (Degussa) hydrophobic silica. Analysis by SEM and image analysis showed the mean SF value to be 133, and the 50% value (from the cumulative distribution curve) to be 129. The toner was then printed in a monocomponent monochrome printer which had been modified to remove the fuser, to allow printing of un-fused images. Unfused print samples were prepared at 1.0 and 2.0 mg/cm^2 using multiple passes through the printer.

The images were then fused off-line using a QEA Fuser-Fixer equipped with a pair of heated oil-less fuser rollers. The fuser speed was set to 20ppm for images printed on paper, and 10ppm for images printed on transparencies for an overhead projector. For the prints on both paper and transparency, no hot offset or paper wrapping was found to occur up to 175°C (the maximum fusion temperature studied)

The samples printed and fused on acetates were examined using a Minolta CM-3600d Haze Meter, according to ASTM D 1003. The results are shown below:

Fusion temperature (°C)	Haze % (H)	
	1 mg/cm^2 print density	2 mg/cm^2 print density
130	29.3	42.5
135	25.6	42.9
140	27.1	40.8
145	26.8	42.0
150	26.2	40.4
155	25.1	38.8
160	25.5	39.5
165	24.4	40.8
170	23.4	40.3
175	23.2	40.0
Haze ratio $H_{(130)}/H_{(160)}$	1.15	1.08

As can be seen the samples show minimal variation in haze with fusion temperature in the range studied.

A separate sample of the toner was then printed in a similar printer, but this time with the fuser unit installed. A print run of 1000 text prints was carried out, and the masses of both the consumed toner, and the toner sent to the waste tray were measured. From this a usage efficiency figure, defined as

[1 –{(mass of toner sent to the waste tray) / (mass of toner consumed)}] x 100

was calculated. The value was 93%.

After a 3000 page print test there was found no noticeable background development on the photoconductor, and no photoconductor filming.

4.2 Toner examples 2-5

Other toners were made and tested in a similar way to Toner 1. The latexes used are listed in Table 1 below, along with the circularity and usage data.

Table 1

Toner	"a" Latex	"b" Latex	Mean circularity (FPIA)	SF (mean)	SF (50% value)	Usage Efficiency (%)
1	a-1	b-1	0.95	133	129	93
2	a-2	b-3	0.96	154	143	96
3	a-2	b-1	0.96	139	135	92
4	a-1	b-2	0.91	161	156	94
5	a-1	b-2	0.91	161	152	94

Throughout the description and claims of this specification, the words "comprise" and "contain" and variations of the words, for example "comprising" and "comprises", mean "including but not limited to", and are not intended to (and do not) exclude other components.

It will be appreciated that variations to the foregoing embodiments of the invention can be made while still falling within the scope of the invention. Each feature disclosed in this specification, unless stated otherwise, may be replaced by alternative features serving the same, equivalent or similar purpose. Thus, unless stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

All of the features disclosed in this specification may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive. In particular, the preferred features of the invention are applicable to all aspects of the invention and may be used in any combination. Likewise, features described in non-essential combinations may be used separately (not in combination).

It will be appreciated that many of the features described above, particularly of the preferred embodiments, are inventive in their own right and not just as part of an embodiment of the present invention. Independent protection may be sought for these features in addition to or alternative to any invention presently claimed.

Claims

1.   A toner for developing an electrostatic image comprising a binder resin, a wax and a colorant, characterised in that the toner is made by flocculating a dispersion of the resin (latex), a dispersion of the wax and a dispersion of the colorant, followed by heating and stirring to form composite particles containing the resin, wax and colorant, and then coalescing these particles above the Tg of the resin, wherein the wax comprises a wax having a melting point of between 50 and 150°C, and the coalescence stage is controlled such that:

(a) the mean circularity of the coalesced particles as measured by a Flow Particle Image Analyser is at least 0.90;

(b) the shape factor (SF) of the coalesced particles is at most 165; and

(c) the wax exists in the coalesced particles in domains of 2 µm or less mean particle size.

2.   A toner according to Claim 1 wherein the mean circularity of the coalesced particles is at least 0.93, preferably at least 0.94.

3.   A toner according to Claim 1 or 2 wherein the shape factor (SF) of the coalesced particles is at most 155, preferably at most 145.

4.   A toner according to any one of Claims 1, 2 or 3 wherein the BET surface area of the particles after the coalescence stage and before any optional blending with surface additives is 0.5-1.5 m²/g, preferably 0.6-1.3 m²/g, and more preferably 0.7-1.1 m²/g.

5.   A toner according to any one of the preceding Claims wherein the resin has a ratio of weight average molecular weight (Mw) to number average molecular weight (Mn) of at least 3, preferably at least 5, more preferably at least 10.

6.   A toner according to any one of the preceding Claims wherein the wax exists in the toner in domains of mean diameter 1.5µm or less.

7.   A toner according to any one of the preceding Claims wherein the latex is prepared from at least one latex with monomodal molecular weight distribution and at least one latex with bimodal molecular weight distribution.

8.   A toner according to Claim 7 wherein the monomodal molecular weight latex is a low molecular weight latex and has a number average molecular weight of from 3000 to 10000, preferably from 3000 to 6000.

9. A toner according to either Claim 7 or 8 wherein the bimodal latex has a weight average molecular weight of from 100,000 to 500,000, preferably from 200,000 to 400,000.

10. A toner according to any one of the preceding Claims wherein the resin comprises a copolymer of (i) a styrene or substituted styrene, (ii) at least one alkyl acrylate or methacrylate and (iii) an hydroxy-functional acrylate or methacrylate.

11. A toner according to any one of the preceding Claims wherein the latex further comprises an ionic surfactant.

12. A toner according to any one of the preceding Claims wherein the wax has a melting point of from 50 to 130°C, preferably from 50 to 110 °C, more preferably from 65 to 85 °C.

13. A toner according to any one of the preceding Claims wherein the wax comprises a wax selected from the group consisting of: a polyethylene wax, a paraffin wax, a Fischer-Tropsch wax and an ester wax, including Carnauba wax.

14. A toner according to any one of the preceding Claims wherein the amount of wax incorporated in the toner is from 1 to 30 wt% based on the total weight of toner, preferably from 3 to 20 wt%, and more preferably from 5 to 15 wt%.

15. A toner according to any one of the preceding Claims wherein the wax dispersion comprises an ionic surfactant.

16. A toner according to any one of the preceding Claims wherein the colorant comprises a pigment.

17. A toner according to any one of the preceding Claims wherein the colorant has been milled with an ionic surfactant.

18. A toner according to Claims 11 and 15 and 17 wherein the ionic surfactant comprised in the latex has the same charge sign as the ionic surfactants comprised in the wax dispersion and the colorant dispersion.

19. A toner according to any of the preceding claims which further comprises a charge control agent.

20. A toner according to claim 19 wherein the charge control agent has been milled with the colorant.

21. A process for forming an image, the process comprising developing an electrostatic image using a toner according to any one of the preceding claims, wherein the haze at a print density of 1.0 mg/cm² is below 40, and the ratio of the values at fusion temperatures of 130 and 160°C is at most 1.5 , preferably 1.3 and more preferably 1.2.

22. A process for the manufacture of a toner according to any one of the preceding claims which comprises the following steps:

    I. preparing a latex dispersion;

    II. preparing a wax dispersion;

    III. preparing a colorant dispersion

    IV. mixing the latex dispersion, wax dispersion and colorant dispersion; and

    V. causing the mixture to flocculate.

23. A process according to claim 22 wherein the latex dispersion comprises an ionic surfactant.

24. A process according to claim 22 or claim 23 wherein the preparation of the latex dispersion comprises mixing together at least one latex with monomodal molecular weight distribution and at least one latex with bimodal molecular weight distribution.

25. A process according to claim 24 wherein the latex with bimodal molecular weight distribution is prepared by a process comprising the successive steps of forming a polymer of high molecular weight distribution followed by forming a polymer of low molecular weight distribution such that the resulting latex comprises composite particles comprising both said low molecular weight polymer and said high molecular weight polymer.

26. A process according to any one of claims 22 to 25 which, prior to step iv, further comprises the step of preparing a charge control agent dispersion, which dispersion is then incorporated in step iv by mixing.

27. A process according to claim 26 wherein the charge control agent is milled with the colorant.

28. A process according to any one of claims 22 to 27 wherein the preparation of the wax dispersion comprises the mixing together of the wax with an ionic surfactant.

29.   A process according to any of claims 22 to 28 wherein the preparation of the colorant dispersion comprises the milling together of the colorant with an ionic surfactant.

30.   A process according to claims 23, 28 and 29 wherein the dispersions of latex, colorant, wax, and charge control agent where present, have the same sign charge on the surfactant.

31.   A process according to claim 30 wherein the surfactant present in the dispersions contains a group which can be converted from an ionic to a non-ionic form and vice versa by adjustment of pH.

32.   A process according to claim 31 wherein the surfactant contains a carboxylic acid group and the dispersions are mixed in step (iv) at neutral to high pH and the flocculation step (v) is then effected by reduction of pH.

33.   A process according to claim 31 wherein the surfactant contains a tertiary amine group and the dispersions are mixed in step (iv) at neutral to low pH and the flocculation step (v) is then effected by increase of pH.

34.   A process according to any of claims 22 to 33 further comprising heating the flocculated mixture obtained after step (v) to form loose aggregates of particle size from 3 to 20 μm.

35.   A process according to claim 34 further comprising heating the aggregates to a temperature above the T_g of the latex to induce coalescence to form toner particles.

36.   A process according to claim 35 further comprising blending the particles with one or more surface additives.

37.   A process according to claim 36 wherein the surface additives comprise one of the following: (i) hydrophobised silica ; (ii) large and small particle size silica (iii) hydrophobised silica and one or both of hydrophobised titania and hydrophilic or hydrophobised alumina ; (iv) large and small particle size silica and one or both of hydrophobised titania and hydrophilic or hydrophobised alumina.

38.   A process for the manufacture of an electroreprographic apparatus and/or a component of the apparatus and/or a consumable for use with the apparatus, the process using a toner as claimed in any of claims 1 to 21.

39.   An electroreprographic apparatus, a component of the apparatus and/or a consumable for use with the apparatus, which comprises a toner as claimed in any of

claims 1 to 21.

40.   An electroreprographic apparatus according to claim 39 which:

    i)   has a developer roller and metering blade ;

    ii)   has a cleaning device for mechanically removing waste toner from a photoconductor ;

    iii)   has a photoconductor that is charged by a contact charging means;

    iv)   uses contact development;

    v)   uses oil-less fusion rollers; and/or

    vi)   is a four colour printer or copier, including a tandem machine.